

CORRELATION OF COOKOFF BEHAVIOUR OF
ROCKET PROPELLANTS WITH
THERMOMECHANICAL AND THERMOCHEMICAL
PROPERTIES

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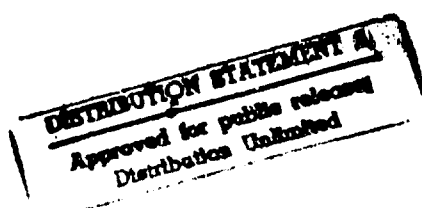
SYHO FERSCHLANDJ. FOURER

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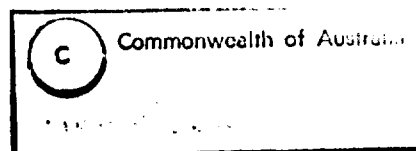
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The fast and slow cookoff behaviour of a series of in-service and research composition rocket propellants have been evaluated using the standard SSCB (based on the NWC design) test, as part of a program in Explosives Ordnance Division (EOD) to develop an extensive insensitive munitions technology base. A modified SSCB test methodology, whereby the pressure output can be measured, was developed to enable a more quantitative measure of the reaction violence and to provide further insight into the cookoff mechanism. The temperature distribution/gradient at various positions and depths in the cylindrical propellant specimen, during fast and slow cookoff, were measured, in order to understand the marked difference in the severity of the response shown by some of the propellants when the heating rate was changed. Pressure and heating rate dependent thermochemical properties and thermomechanical properties of the propellants were measured and correlated with cookoff behaviour.

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Telephone: (03) 246 8111

Fax: (03) 246 8999

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Authors

S.Y. Ho



Sook Ying Ho graduated from the University of Queensland with a BSc (Hons) in 1979 and a PhD in polymer physics in 1984. She joined Explosives Ordnance Division, MRL Salisbury in 1985 after working at the Department of Science and Technology in Canberra. She has worked in the areas of high strain rate mechanical properties, impact ignition mechanisms and cookoff behaviour of rocket and gun propellants, in relation to Insensitive Munitions, and Fracture Mechanics and viscoelasticity of energetic and inert materials for the structural analysis of rocket motors. From August 1989 to November 1990, she was a visiting scientist at the Royal Armament Research and Development Establishment in Waltham Abbey, U.K., where she was involved in the development of a modified Fracture Mechanics theory for non-linear viscoelastic materials, aimed at service life prediction of rocket motors.

T. Ferschl



Tony Ferschl completed his fitting and turning apprenticeship at DSTO Salisbury in 1980 and continued to work in the mechanical workshops. In 1989 he completed an Associate Diploma in mechanical engineering and joined Explosives Ordnance Division, MRL Salisbury in 1989 where he provides technical support in the conduct of small-scale cookoff tests, shotgun test and robotic dissection of rocket motors.

J. Foureur



John Foureur joined EOD/MRL in 1986 after completing 21 years service with the Royal Australian Airforce where his main responsibilities are the maintenance and repair of aircraft. Since joining DSTO he has completed an associate diploma in electronic engineering and has been involved in the ballistic performance testing of rocket motors, and electronic circuitry repair.

Contents

1. INTRODUCTION	7
2. EXPERIMENTAL	9
2.1 Materials	9
2.2 SSCB Test	10
2.3 Thermomechanical Measurements	10
2.4 Thermal Measurements	12
3. RESULTS AND DISCUSSION	12
3.1 Cookoff Response of Propellants	12
3.2 Temperature Distribution as a Function of Time	20
3.3 Thermomechanical Properties and Relation to Cookoff Behaviour	21
3.4 Thermochemical Properties and Relation to Cookoff	26
4. CONCLUSIONS	32
5. ACKNOWLEDGEMENT	33
6. REFERENCES	33

Correlation of Cookoff Behaviour of Rocket Propellants with Thermomechanical and Thermochemical Properties

1. Introduction

Insensitive Munitions (IM), defined in paragraph 6 of the draft Defence Instruction General [DI(G)] on "Insensitive Munitions Policy and Implementation" [1], is an area which is assuming significant importance in Australia. The Australian Defence Force (ADF) is in the process of adopting an official policy on IM promulgated through a DI(G), currently being revised for final submission. Explosive ordnance (EO) in inventory and those being introduced into service are to be assessed against the IM response criteria listed in Annex A of the DI(G) [1]. The potential threat areas in which munitions are required to meet IM criteria include:

- (1) Fast cookoff (fuel fire)
- (2) Slow cookoff
- (3) Bullet impact
- (4) Fragment impact
- (5) Spall impact
- (6) Shaped charge jet impact
- (7) Electrostatic discharge
- (8) 12 metre safety drop
- (9) Sympathetic detonation

The first four IM qualification tests are mandatory, the pass criteria being "no response more severe than burning".

The RAN is the most proactive Service for adoption of IM. Slow and fast cookoff are technology shortfall areas highlighted in a recent RAN discussion paper on "Insensitive Munitions Acceptance Criteria and Tests" [2]. For example, realistic heating rates appropriate to a given threat scenario and hazard response criteria need to be identified. One of the aims of the present study is to obtain a better fundamental understanding of cookoff mechanisms, in order to help alleviate these technology gaps.

Small-scale laboratory tests that can predict the response of energetic materials to cookoff are very desirable as they provide a cost effective, simple and very quick means of assessing the response of the energetic component of the munition to cookoff. Small-scale tests are also convenient for conducting fundamental studies of the important factors that control cookoff induced reactions.

A super small-scale cookoff bomb (SSCB) test facility, based on the Naval Weapons Centre (NWC) design [3], has recently been established at MRL [4] for assessing the response of explosives to fast and slow cookoff. In the present study, the cookoff behaviour of several typical in-service and research composition rocket propellants was assessed using the SSCB test, as part of a program to develop an extensive IM technology base on solid propellants. A modified version of the standard SSCB test was also used here to enable a more quantitative measure of the reaction violence (via a pressure transducer) to be obtained, and thus provide a more scientific basis for predicting the hazard response of munitions. In the standard SSCB test, the reaction violence is determined mainly by the extent of damage to the vessel. However, it is often difficult to assess the severity of the test response, because the boundaries between the various levels of reaction are not distinct. The difficulty can be partially eliminated by using the modified SSCB, where the pressure/energy output is measured. Modification of the standard SSCB did not alter the test response or the reaction temperature and time.

Although the propellant size/geometry used in the SSCB test is much smaller than the propellant charges used in the in-service rocket motor, this small-scale test can be expected to be useful in ranking the response of different propellants. It should be noted that the critical diameters for a deflagration-to-detonation transition (based on similar propellants) of the HTPB/RDX, HTPB/PETN and cast double base (CDB) propellants used in this study are smaller than the diameter of the specimen used in the SSCB test, but the HTPB/AP and HTPB/AN propellants have much larger critical diameters. The critical diameters of the HTPB/AP propellants exceed 200 mm, i.e. larger than the charge diameter of most in-service rocket motors in the ADF inventory. A self-sustaining detonation reaction cannot therefore be achieved in full- and small-scale testing of these propellants.

Although there have been numerous studies on the characterization of the fast and slow cookoff behaviour of energetic materials [3-6], little detailed information is available on the pressure and temperature dependence of the physico-mechanical and chemical kinetic parameters of the energetic material and their relation to cookoff behaviour. The development of satisfactory prediction methodologies and modelling tools requires the physico-mechanical and chemical kinetic properties to be known as a function of temperature, pressure and heating rate. For example, it is important to know the phase changes in the propellant as a function of temperature because the grain geometry is dependent on the phase/state changes with temperature. In this study, the cookoff behaviour of rocket propellants, with widely different thermomechanical and thermochemical properties, was assessed using the standard and modified SSCB tests. The

cookoff behaviour of these propellants was correlated with pressure and heating rate dependent chemical kinetics and thermomechanical properties. The propellants tested in these small-scale tests will also be used in motors in full-scale testing, to enable a direct comparison to be made of the relevance of the SSCB test to cookoff effects in rocket motors.

2. Experimental

2.1 Materials

The composite propellant types, cast double base propellant (CDB), and their compositions are listed in Table 1. Heats of explosion (calorimetric values) of these propellants were calculated from the weight fraction and calorimetric value of each of the propellant ingredients (estimated from the heats of formation and combustion at constant volume) and are listed in Table 2.

Table 1: Propellant compositions

Propellant Type	Binder Prepolymer	Curative	Plasticizer (Weight %)	Oxidiser ² (Weight %)
Composite				
HTPB/AP (20/80)	Hydroxyterminated polybutadiene	DDI		Ammonium perchlorate (50%)
Hard HTPB/AP ¹ (12/88)			4.8	Ammonium perchlorate (55%)
Soft HTPB/AP ¹ (12/88)			8.0	Ammonium perchlorate (55%)
HTPB/PETN (20/80)		IPDI		Pentaerythritol tetranitrate (50%)
HTPB/RDX (20/80)		DDI		Cyclotrimethylene trinitramine (50%)
Double Base				
CDB	Nitrocellulose-Nitroglycerine (42/46 weight %)			

Note 1. Dioctyladipate was used as the plasticizer.

2. Oxidiser particle coarse/fine ratio = 65/35; coarse -200 μm ,
fine -16 μm .

Table 2: Heat of explosion of propellants

Propellant Type	Heat of Explosion (kJ kg ⁻¹)
Hard HTPB/AP (12/88)	6290
Soft HTPB/AP (12/88)	6259
HTPB/AP (20/80)	4611
HTPB/RDX (20/80)	2286
HTPB/PETN (20/80)	2943
HTPB/AN (20/80)	2710
CDB	4425

The thermochemical and mechanical properties of these propellants were varied by varying the oxidiser type and loading level, and the plasticizer level. Hydroxy-terminated polybutadiene (HTPB), cured with IPDI or DDI, was used as the binder in all the rubbery composite propellants. The oxidiser particle size and coarse/fine ratio (65/35) were approximately the same for all the composite propellants studied here. All the propellants were made by standard processing techniques as described previously [7,8].

The processed propellants were machined into cylindrical pellets of 16 mm diameter and 64 mm length, with a mass of approximately 20 g, for the SSCB test.

2.2 SSCB Test

The design of the standard SSCB test has been described in detail in reference [3]. Tests were conducted on all the samples at both fast (ca. $1.2^{\circ}\text{C s}^{-1}$) and slow (ca. $0.1^{\circ}\text{C s}^{-1}$) heating rates. For these tests, the measured temperature in the slot for the thermocouple (Type K) in the aluminium liner was assumed to be similar to the propellant surface temperature. This assumption is valid at the slow heating rate, where the differences between the measured temperature and the propellant surface temperature were minimal, there never being more than 2°C difference between these two locations at any one time (see Section 3.2).

For all the propellants, tests were also conducted using a modified SSCB vessel which enables the pressure developed during cookoff to be measured. The standard test was modified by replacing the sealing plug from the top of the test assembly with a stainless steel pipe which connects to a pressure transducer, Kistler type 6207A. The quartz pressure transducer used in this study has a rise time of $1\ \mu\text{s}$ and a sensitivity of $\sim 1.2\ \text{pC/bar}$, and can only measure dynamic or quasistatic pressures. A shield was used to mount the pressure transducer and to protect it from the blast. A diagram of the modified SSCB is shown in Fig. 1.

Studies on the temperature gradient/distribution in some of the propellants during fast and slow cookoff were conducted by placing thermocouples at six different locations within the SSCB. The thermocouple positions are indicated in Fig. 2. The thermocouples were connected to a Datalogger 500 data logger which has 30 analog channels.

2.3 Thermomechanical Measurements

Dynamic Mechanical (DMTA) properties of the propellants were measured using a Rheometrics Mechanical Spectrometer, Model RDA2 [9]. Measurements were made in a forced shear mode using a rectangular torsion geometry. The analysis was made over a temperature range of -120°C to 100°C using a temperature step size of 3°C and a test frequency of $0.1\ \text{rad s}^{-1}$. The glass transition temperature, T_g , was determined from the temperature at which the shear loss modulus, G'' , was a maximum.

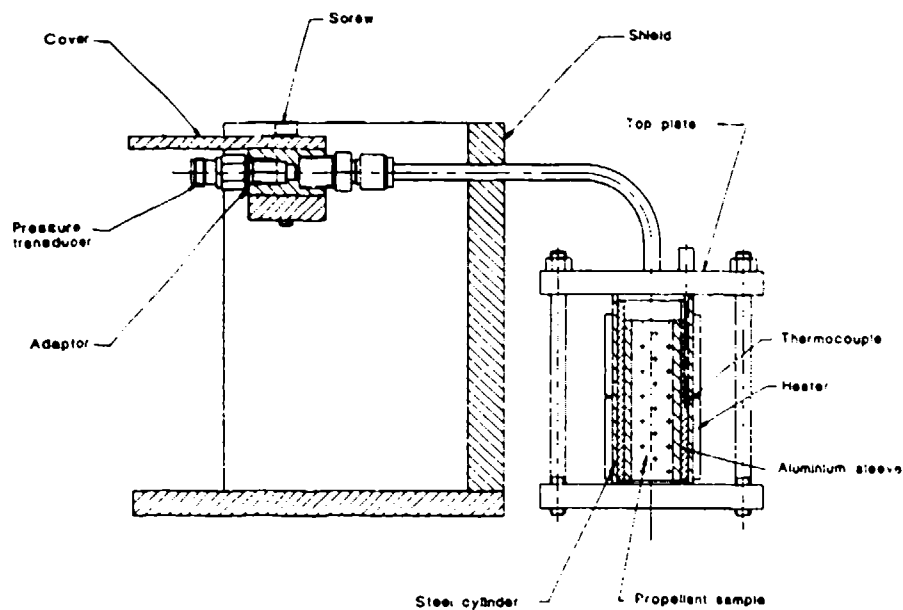


Figure 1: Modified super small-scale cookoff bomb

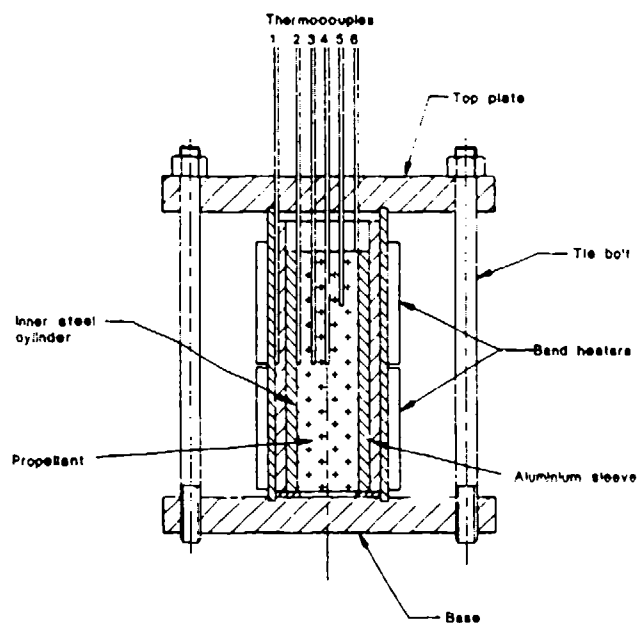


Figure 2: Thermocouple locations in SSCB

2.4 Thermal Measurements

Thermal measurements were conducted using a Du Pont model 910 Differential Scanning Calorimeter (DSC) over the pressure range 0.1 to 5.2 MPa. The samples (2 mg to 4 mg) were heated over the temperature range 30°C to 400°C at heating rates of 5°C min⁻¹ and 20°C min⁻¹.

Kinetic parameters of the thermal decomposition were calculated from a single DSC thermogram using the following equations to represent the extent of decomposition and their temperature dependence

$$\ln k = -\ln (da/dt) + n \ln (1-a) \quad (1)$$

and $k = A e^{-(E_a/RT)} \quad (2)$

where k is the rate constant, da/dt is the rate of reaction = $dH/dt \times 1/A_T$ (dH/dt = peak height at a given time and A_T = total area under the thermogram peak), a is the degree of conversion ($a = 1 - A_T \times H$, where H is the area under the thermogram peak from time = 0 to a given time = t), n is the reaction order, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature. Combining equations (1) and (2) gives

$$\ln (da/dt) = n \ln (1-a) - E_a/RT + \ln A \quad (3)$$

Equation (3) has the form $f = f_0 + f_1x + f_2y$ where $\ln (da/dt)$ is the dependent variable, $\ln (1-a)$ and $1/T$ are the independent variables and n , E_a/R and $\ln A$ are the constants f_1 , f_2 and f_3 respectively. Hence, the best values of n , E_a/R and $\ln A$ can be determined by a multilinear regression analysis.

3. Results And Discussion

3.1 Cookoff Response of Propellants

The cookoff behaviour of the propellants studied here have been assessed using the standard and modified SSCB test. Some still frames from a normal speed (24 frames per second) video taken during small-scale cookoff testing of the hard HTPB/AP (12/88) propellant are shown in Fig. 3a-f. They show the sequence of events during small-scale cookoff testing. The test response here is an explosion. The fast and slow cookoff test responses of the propellants are summarized in Table 3. Reaction temperature and time, at the slow and fast heating rates, are shown in the temperature-time profiles in Figs. 4 and 5.

The propellants can be ranked, in decreasing order, according to their reaction violence as follows (propellants in the same box have a similar ranking).

Fast Heating Rate	Slow Heating Rate
Hard HTPB / AP (12.88)	Hard HTPB / AP (12.88)
HTPB / PETN (20.80) HTPB / AP (20.80)	HTPB / PETN (20.80) HTPB / RDX (20.80)
Soft HTPB / AP (12.88)	Soft HTPB / AP (12.88) HTPB / AP (20.80)
HTPB / RDX (20.80)	CDB HTPB / AN (20.80)
CDB HTPB / AN (20.80)	

In general, the trends are similar at the fast and slow rates except for the HTPB / RDX (20.80) propellant which showed a violent deflagration/explosion reaction at the slow rate but a burning reaction at the fast rate. The very marked difference in the severity of test response shown by the HTPB / RDX (20.80) propellant, when the heating rate was changed, may be explained by the different temperature distribution in this propellant during fast and slow cookoff (see Section 3.2)

Table 3. Cookoff response (SSCB) of propellants

Propellant Type	Heating Rate	Temperature (°C)	Time (min)	Response
Hard HTPB / AP (12.88)	Fast	328	9.8	Deflagration
	Slow	241	190.6	Deflagration, Explosion Deflagration, Explosion Explosion
Soft HTPB / AP (12.88)	Fast	327	10.2	Deflagration
	Slow	231	461.2	Deflagration
HTPB / AP (20.80)	Fast	339	10.8	Deflagration, Explosion Deflagration Explosion
	Slow	256	>700	Deflagration
HTPB / RDX (20.80)	Fast	277	7.0	Burning Burning, Mild burning
	Slow	200	36.3	Deflagration Deflagration, Explosion
HTPB / PETN (20.80)	Fast	206	4.5	Deflagration Deflagration, Explosion
	Slow	171	21.7	Deflagration Explosion
HTPB / AN (20.80)	Fast	371	7.2	Mild burning Burning
	Slow	238	36.3	Mild burning, Burning
CDB	Fast	209	4.3	Mild burning, Burning Burning
	Slow	161	19.8	Mild burning Mild burning

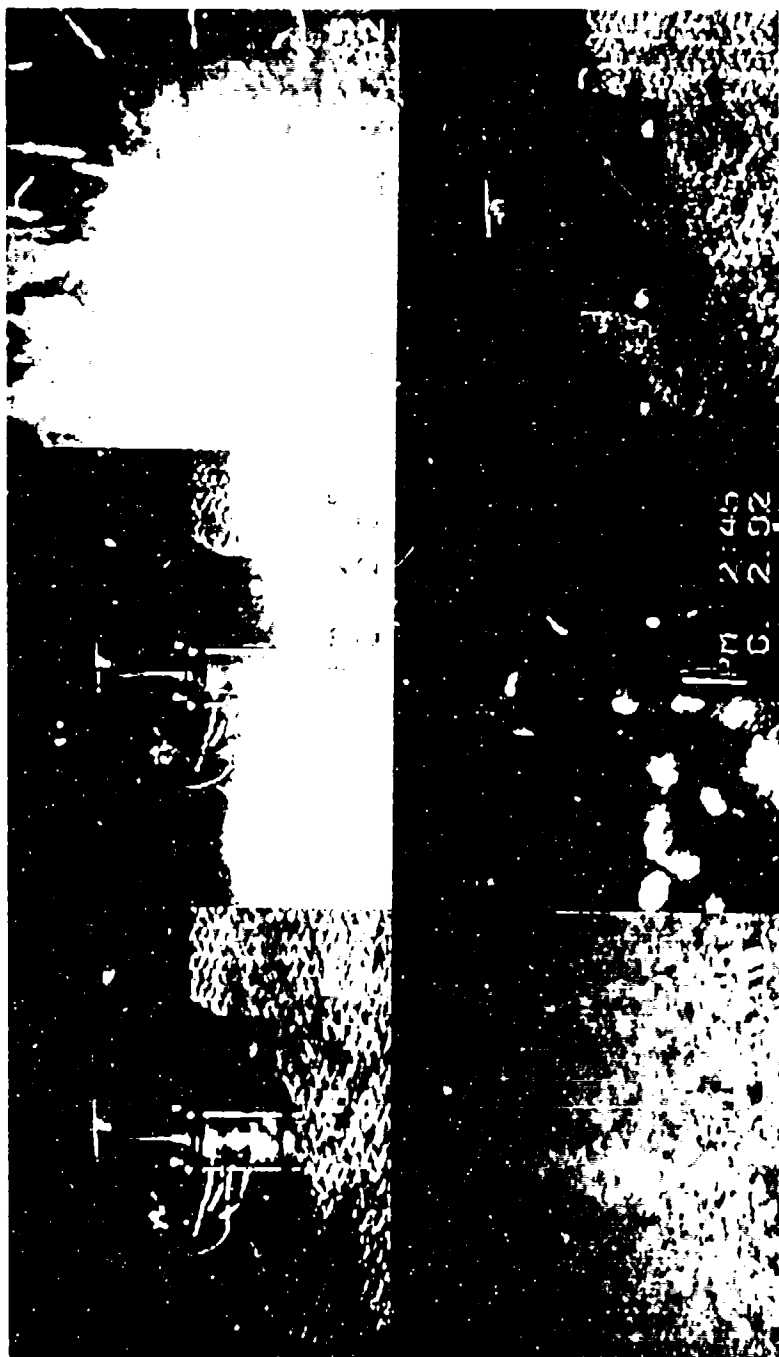


Figure 3. Sequence of events during small-scale cooking

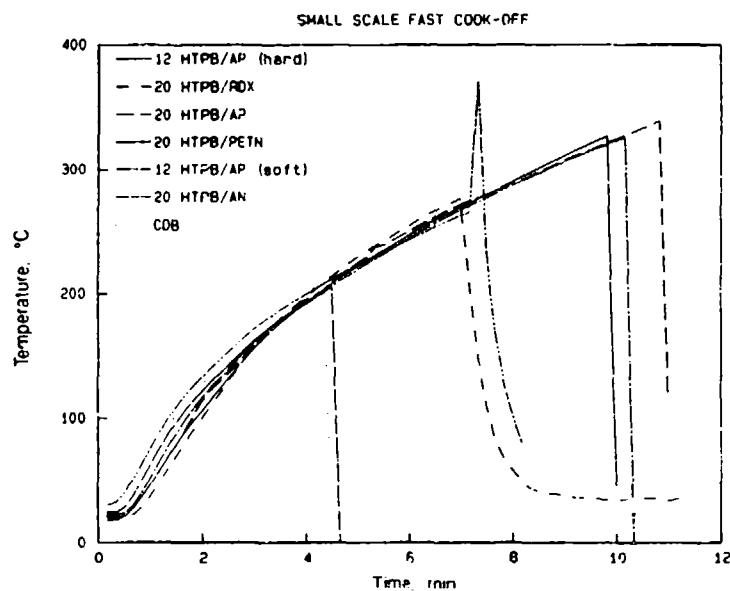


Figure 4: Temperature-time profile of propellants, fast heating rate

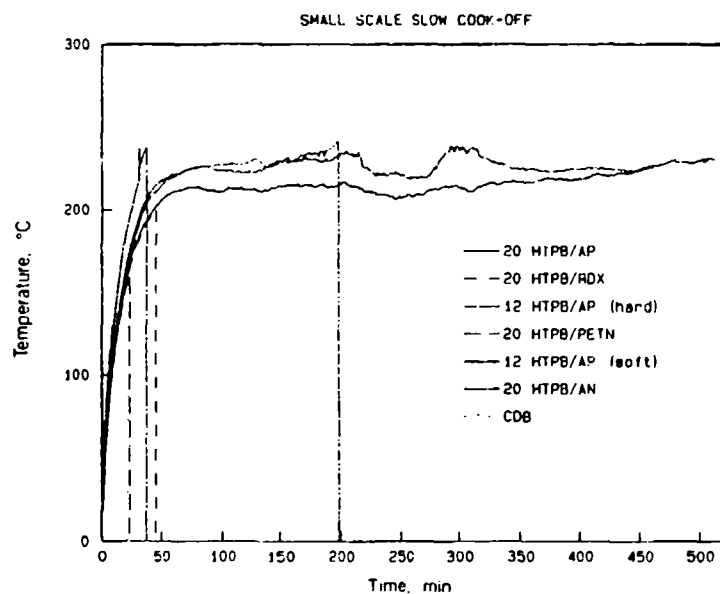


Figure 5: Temperature-time profile of propellants, slow heating rate

At both the fast and slow heating rates, the hard HTPB/AP (12:88) propellant showed the most violent response, presumably a result of its relatively high heat of explosion (see Table 2), which is one of the many factors governing cookoff response. When the plasticizer level of the HTPB/AP (12:88) propellant was increased, the severity of the response was moderated. The soft HTPB/AP (12:88) propellant has more flexible/extensible characteristics but its calorimetric value is almost identical to the hard HTPB/AP (12:88) propellant. The mechanism by which plasticizers decrease the level of test response is not well understood. Determination of the thermomechanical properties of these propellants (ambient to 120°C) using DMTA showed that the highly plasticized propellant is less viscous at higher temperatures (see Section 3.3). The less viscous propellant, because of its greater flow, is also harder to initiate i.e. longer initiation time (Figs. 4 and 5).

The CDB propellant showed a surprisingly mild response at both heating rates, although its calorimetric value is similar to the HTPB/AP (20:80) propellant (see Table 2). The mild response may be related to the highly plasticized nature of this CDB propellant, which contains 45 weight % of nitroglycerine in the formulation. The HTPB/AN (20:80) propellant also showed a comparatively mild cookoff response at both heating rates. This may be due to its favourable thermal properties, where a large part of the decomposition is endothermic (see Section 3.4 and Fig. 10d).

The pressure-time profiles of the propellants, at the fast and slow heating rates, are illustrated in Fig. 6a and b (note that the start of the pressure-time plots have been offset for clarity). In this new methodology, using the pressure-time data from the modified SSCB test, the initial rate of pressure rise (i.e. the initial slope of the pressure-time plot) is related to the rate of energy release and gives some indication of the likelihood of a violent reaction occurring. The impulse (area under the pressure-time plot) is a measure of the total energy released during the reaction and therefore, must also be related to the extent of damage. Average values from 2 - 3 measurements for the peak pressure, initial pressure rise (dp/dt), and impulse are listed in Table 4. It is important to note that, depending on the propellant, the time scale of the measured pressure is 80 to 700 microseconds i.e. the time taken for pressure rise and buildup is very small in comparison to the time taken to deform/damage the SSCB test assembly. Thus, peak pressures above the calculated burst pressure of the SSCB test assembly (ca. 73 MPa) can be measured.

At both the fast and slow heating rates, the initial pressure rise for an explosion is relatively high (dp/dt is ca. 3×10^6 MPa.s⁻¹) and the initiation pressure and impulse exceed 750 MPa and 0.52 MPa.s respectively (e.g. the hard HTPB/AP (12:88) propellant). For test responses which lie between deflagration and explosion (e.g. HTPB/AP (20:80) and HTPB/PETN (20:80) propellants at the fast heating rate), the initiation pressure is 300 to 500 MPa and the impulse is 0.075 to 0.096 MPa.s. For deflagration reactions, the measured impulse (e.g. 0.055 MPa.s for the soft HTPB/AP (12:88) propellant at the fast heating rate) is lower than that for a deflagration/explosion reaction but the peak pressure is in the same range (300 to 500 MPa).

Table 4: Measured pressures from modified SSCB

Propellant Type	Heating Rate	Peak Pressure (MPa)	Impulse (MPa.s)	dP/dt (MPa.s ⁻¹)
Hard HTPB/AP (12:88)	Fast Slow	>800	$>6.0 \times 10^{-1}$	3.5×10^6
Soft HTPB/AP (12:88)	Fast Slow	460	5.6×10^{-2}	0.28×10^6
HTPB/AP (20:80)	Fast Slow	355, 362	9.1×10^{-2}	2.3×10^6
HTPB/RDX (20:80)	Fast Slow	130 505	3.5×10^{-2} 5.6×10^{-1}	3.3×10^6 6.6×10^6
HTPB/PETN (20:80)	Fast Slow	432 164	7.6×10^{-2} 6.9×10^{-2}	1.7×10^6 5.8×10^6
HTPB/AN (20:80)	Fast Slow	425	3.5×10^{-4}	1.2×10^9
CDB	Fast Slow	55	1.3×10^{-2}	2.6×10^4

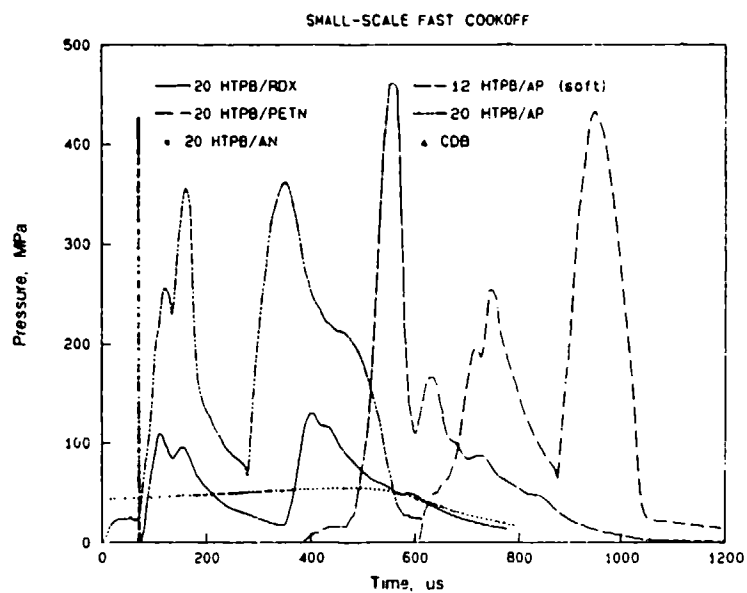
The modified SSCB test is useful in separating propellants which showed similar damage to the SSCB test assembly. For example, the HTPB/RDX (20:80), HTPB/AN (20:80) and CDB propellants all gave burning reactions at the fast rate, however, the impulse indicated that the RDX propellant gave a more violent reaction compared to the other two propellants (see Fig. 6a and Table 4). It is interesting to note that the HTPB/AN (20:80) propellant gave a relatively high peak pressure but the impulse was very low. On the other hand, the CDB propellant gave a very low peak pressure over a much longer time.

In assessing the cookoff hazard of rocket motors, it is important to have not only some indication of the severity of the response, but also to know when to expect a reaction. Thus, a second criteria for cookoff response is the ease of initiation. This is given by the reaction temperature and time obtained from the temperature-time profile. In contrast to explosives, where the reaction time and temperature are not very different for different compositions (based on the same explosive with different binders [3 - 6]), these parameters differ significantly for the different classes of propellants and for similar propellants with different binder to oxidiser weight ratios (Table 3). The propellants are ranked according to their ease of initiation, at the fast and slow heating rates, as follows (propellants in the same box having a similar ranking):

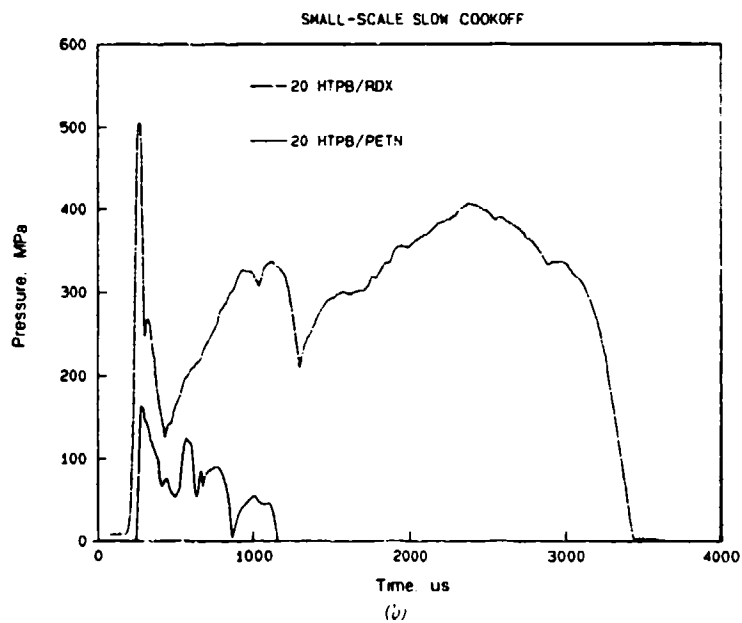
INITIATION TEMPERATURE		INITIATION TIME	
Fast Rate	Slow Rate	Fast Rate	Slow Rate
CDB	CDB	CDB	CDB
HTPB/PETN (20 80)			
	HTPB/PETN (20 80)	HTPB/PETN (20 80)	HTPB/PETN (20 80)
HTPB/RDX (20 80)	HTPB/RDX (20 80)	HTPB/RDX (20 80)	HTPB/RDX (20 80) HTPB/AN (20 80)
Hard HTPB/AP (12 88) Soft HTPB/AP (12 88)	HTPB/AN (20 80)	HTPB/AN (20 80)	
HTPB/AP (20 80)	Soft HTPB/AP (12 88)	Hard HTPB/AP (12 88)	Hard HTPB/AP (12 88)
HTPB/AN (20 80)	Hard HTPB/AP (12 88)	Soft HTPB/AP (12 88)	Soft HTPB/AP (12 88)
	HTPB/AP (20 80)	HTPB/AP (20 80)	HTPB/AP (20 80)

The same trends were observed for the initiation times at both the fast and slow heating rates. However, the trends for the initiation temperatures are slightly different for the two heating rates, probably a result of the non-uniform temperature distribution across the specimen during fast cookoff.

For the composite propellants, the ease of initiation is dominated by the oxidiser type. The PETN and CDB propellants react very quickly and initiate at very low temperatures compared to the AP propellants, due to their comparatively low thermal stability (see Section 3.4 and Table 5). The AP propellants are the hardest to initiate. Increasing the plasticizer level substantially increased the reaction time but the initiation temperature was not altered.



(a)



(b)

Figure 6: Pressure-time profile of propellants. (a) fast heating rate, (b) slow heating rate.
 Note: Start of pressure-time plots have been offset for clarity.

Table 5: Melting temperature (T_m) and onset temperature for decomposition (ambient pressure) from DSC

Propellant Type	Heating Rate ($^{\circ}\text{C min}^{-1}$)	Melting Temperature ($^{\circ}\text{C}$)	First Onset Temperature ($^{\circ}\text{C}$)	Second Onset Temperature ($^{\circ}\text{C}$)
HTPB/AP (20:80)	5	-	294	366
	20	-	336	397
Hard HTPB/AP (12:88)	5	-	296, 317	372
	20	-	329, 345	385
Soft HTPB/AP (12:88)	5	-	290, 313	339, 345
	20	-	326, 348	365, 370
HTPB/RDX(20:80)	5	198	222	-
	20	205	243	-
HTPB/PETN(20:80)	5	129	190	-
	20	140	204	-
HTPB/AN(20:80)	5	126, 167	237	-
	20	127, 169	267	-
CDB	5	-	196	-
	20	-	221	-

3.2 Temperature Distribution as a Function of Time

The temperature distribution within the specimen as a function of time, at the fast and slow heating rates, was measured for the HTPB/RDX (20:80) and HTPB/AP (20:80) propellants. The HTPB/RDX (20:80) propellant showed a marked difference in the severity of the test response when the heating rate was changed. Temperature distributions as a function of time and, the radial and axial temperature profiles are illustrated in Figs. 7 and 8.

In general, at the slow heating rate, almost uniform temperature distribution across the specimen was achieved after the first 30 minutes; there was never more than 2°C difference between the propellant surface and the Al liner of the SSCB apparatus at any one time. For both heating rates, the temperature difference in the axial direction is insignificant (less than 2°C to 3°C at any one time), except on the propellant surface where there is an air gap and heat loss by convection through the top end of the SSCB apparatus can occur (see temperature profiles for thermocouple positions 3 of 5 and 2 of 6 in Figs. 7a - d). On the other hand, the radial temperature distribution is significant and highly dependent on the heating rate.

Our results clearly show that the slow heating rate produced a cookoff reaction beginning at the centre of the propellant (Fig. 8a and b). For the HTPB/RDX (20:80) propellant, the temperature at the centre became higher than the outer surface temperature several minutes before initiation, due to self heating of the propellant. Reactions originating at the centre may be expected to be more violent than those beginning at the outer surface because of self confinement and decreased heat loss. Reactions which originate from the outer surface are more

likely to result in early rupture leading to venting of the test vessel and pressure release.

The fast heating rate produced a cookoff reaction beginning at the outer surface of the propellant (see Fig. 8c and d). Temperatures at the surface (thermocouple positions 2 and 6) are much higher than temperatures near the centre of the propellant (thermocouple positions 3, 4 and 5). This difference was almost 100°C and 30°C to 40°C for the HTPB/RDX (20:80) and HTPB/AP (20:80) propellants respectively. The much lower temperature at the centre compared to the outer surface of the HTPB/RDX (20:80) propellant can explain its surprisingly mild test response at the fast heating rate, because of early rupture and venting of the SSCB test vessel.

3.3 Thermomechanical Properties and Relation to Cookoff Behaviour

A typical DMTA spectrum of a HTPB/AP propellant is shown in Fig. 9. Dynamic shear storage and loss moduli (G' and G'' respectively) and loss tangent ($\tan \delta$) are plotted as a function of temperature. The loss tangent plot shows two major relaxations - the low temperature glass transition at around -79°C to -82°C, and a very broad high temperature transition (designated T_g here) in the temperature range of -35°C to -15°C. They correspond to relaxation of the soft segments (composed primarily of the HTPB prepolymer) and of the hard segments (composed mainly of sequences of the isocyanate curative reacted with the crosslinker or extender) respectively. The incompatibility of the hard and soft segments and subsequent phase separation into separate domains is well documented for block copolymers and poly(butadiene-urethane) rubbers [7-9, 11-13].

The G' vs. temperature plot of a typical HTPB/AP propellant shows that in the temperature range -130°C to -80°C the shear modulus is ≈ 1 GPa and the propellant is in a glassy state, exhibiting brittle mechanical behaviour. In the temperature range -30°C to 70°C, the shear modulus drops to 1 to 10 MPa, indicative of rubber-like behaviour. Above 70°C, permanent deformation has occurred and the propellant is in a rubbery-viscous state. These phase changes with temperature would have some influence on the heat transfer characteristics and geometry of the specimen [14], and must be taken into account when modelling the cookoff response.

Comparison of the DMTA spectra of the HTPB/AP (12:88) propellants with different plasticizer levels indicate that the $\log G''$ vs. temperature plot for the more highly plasticized propellant exhibits lower loss shear moduli, and thus, lower viscosities ($\eta' = G''/\omega$, where η' is the in-phase viscosity and ω is the frequency). Therefore, plasticizers may be expected to moderate the cookoff response by decreasing the viscosity or increasing the flow of the material. A more detailed description of the effect of plasticizer level on the thermomechanical properties and cookoff response of propellants will be described in a later paper.

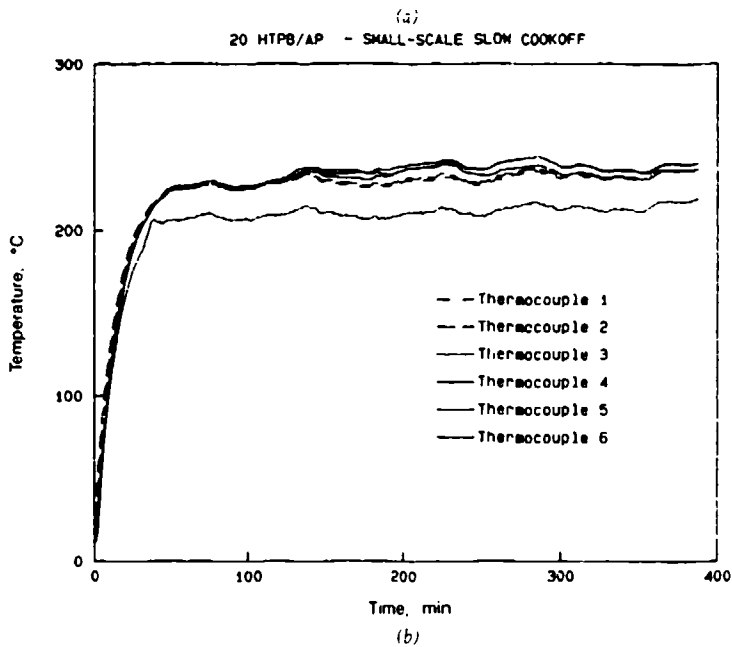
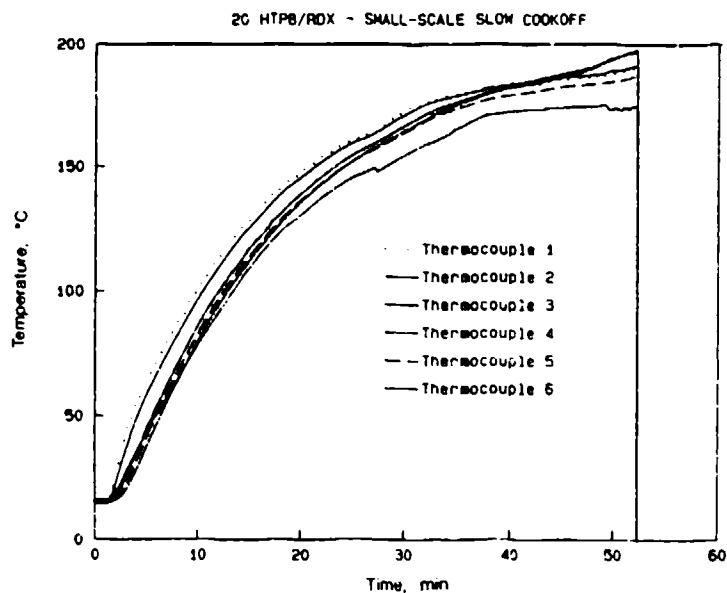


Figure 7: Temperatures measured at six locations in the SSCB as a function of time, (a) HTPB/RDX (20:80), slow heating rate, (b) HTPB/AP (20:80), slow heating rate, (c) HTPB/RDX (20:80), fast heating rate, (d) HTPB/AP (20:80), fast heating rate.

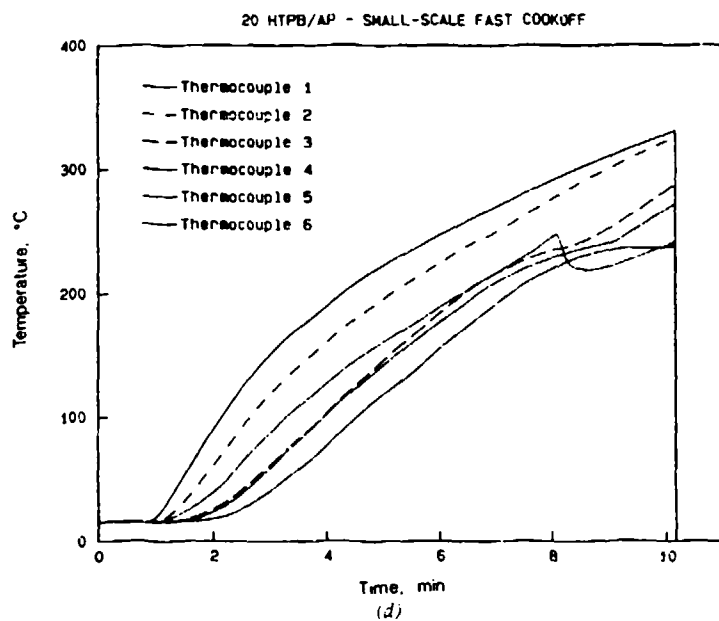
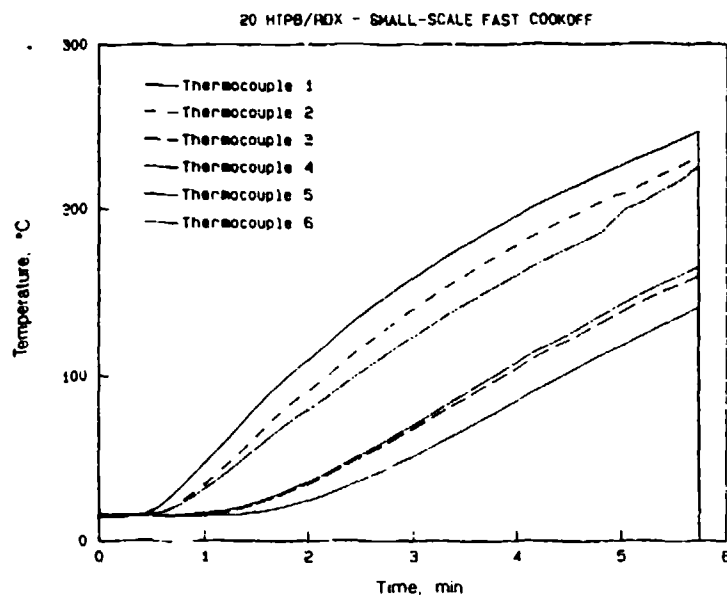
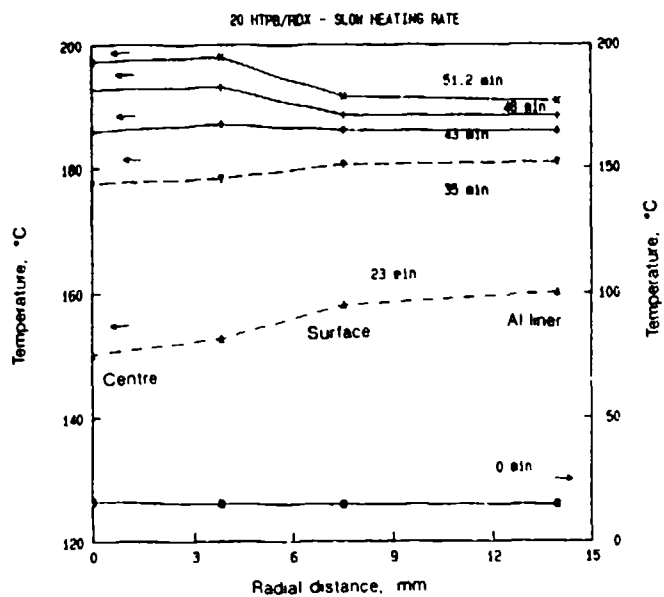
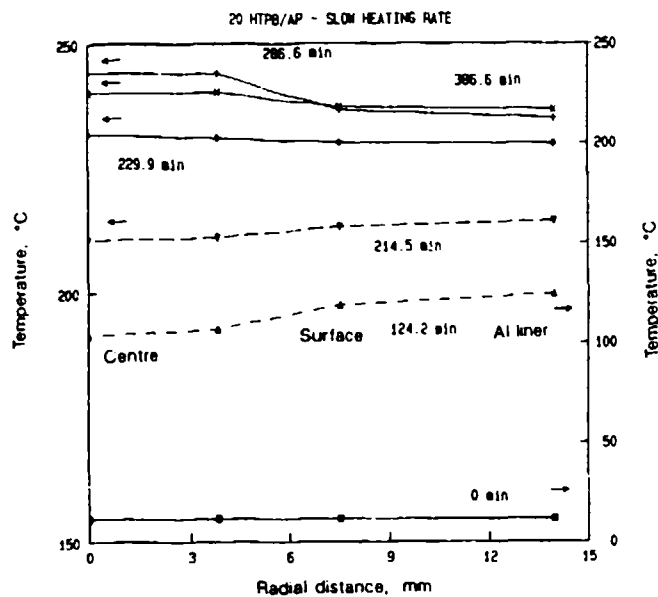


Figure 7 Cont: Temperatures measured at six locations in the SSCB as a function of time, (a) HTPB/RDX (20:80), slow heating rate, (b) HTPB/AP (20:80), slow heating rate, (c) HTPB/RDX (20:80), fast heating rate, (d) HTPB/AP (20:80), fast heating rate.

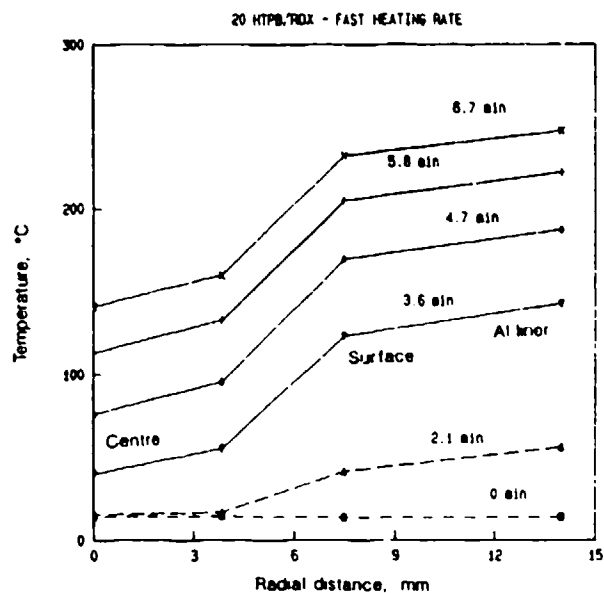


(a)

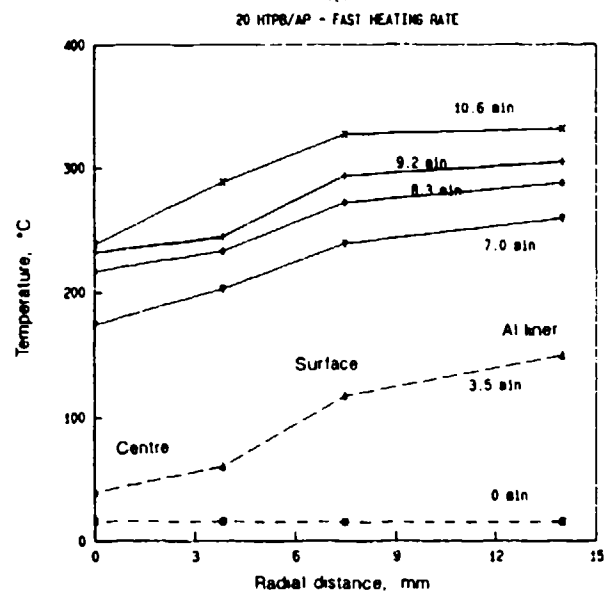


(b)

Figure 8: Temperatures measured at several locations in the SSCB as a function of radial distance, (a) HTPB/RDX (20:80), slow heating rate, (b) HTPB/AP (20:80), slow heating rate (c) HTPB/RDX (20:80), fast heating rate, (d) HTPB/AP (20:80), fast heating rate.



(c)



(d)

Figure 8 Cont: Temperatures measured at several locations in the SSCB as a function of radial distance. (a) HTPB/RDX (20:80), slow heating rate, (b) HTPB/AP (20:80), slow heating rate (c) HTPB/RDX (20:80), fast heating rate, (d) HTPB/AP (20:80), fast heating rate

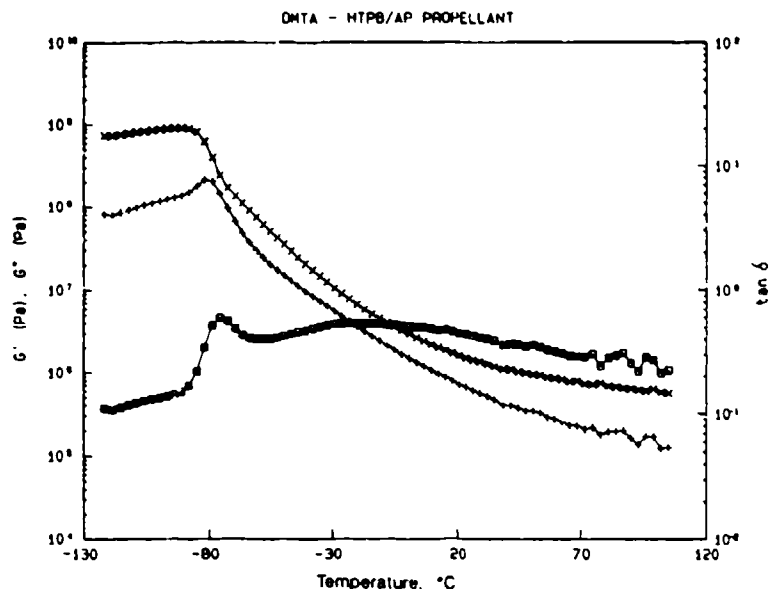


Figure 9: Viscoelastic spectrum of a HTPB/AP propellant (x) G' , (+) G'' , (□) $\tan \delta$

3.4 Thermochemical Properties and Relation to Cookoff Behaviour

Thermal Decomposition

The thermal decomposition, at ambient pressure, of propellants similar to the ones studied here have been described in detail in reference 10. Melting and onset temperatures for the thermal decomposition, at 5°C and $20^\circ\text{C min}^{-1}$, are listed in Table 5.

Typical DSC traces are shown in Fig. 10a-f. Propellants containing AP as an oxidiser undergo a two-step degradation process at ambient pressure. The initial degradation occurring in the temperature range 210°C to 230°C has been attributed to the thermal decomposition of the oxidiser and the major decomposition, occurring in the temperature range 300°C to 400°C , is due to a number of reactions occurring simultaneously which include decomposition of the polymeric binder and further decomposition of the oxidiser [10].

At ambient pressure, the HTPB/PETN (20:80) and HTPB/RDX (20:80) propellants undergo thermal decomposition in the temperature range 150°C to 225°C and 209°C to 230°C respectively. Unlike the AP propellants, only one major degradation process was observed for these propellants. The AN propellant did not show an endotherm at the melting point, ca. 170°C , of the oxidiser. This may be due to the ability of AN to form a stable liquid at its melting point [15]. However, above the melting point of AN (see Fig. 10d), a large part of the decomposition of the AN propellant is endothermic.

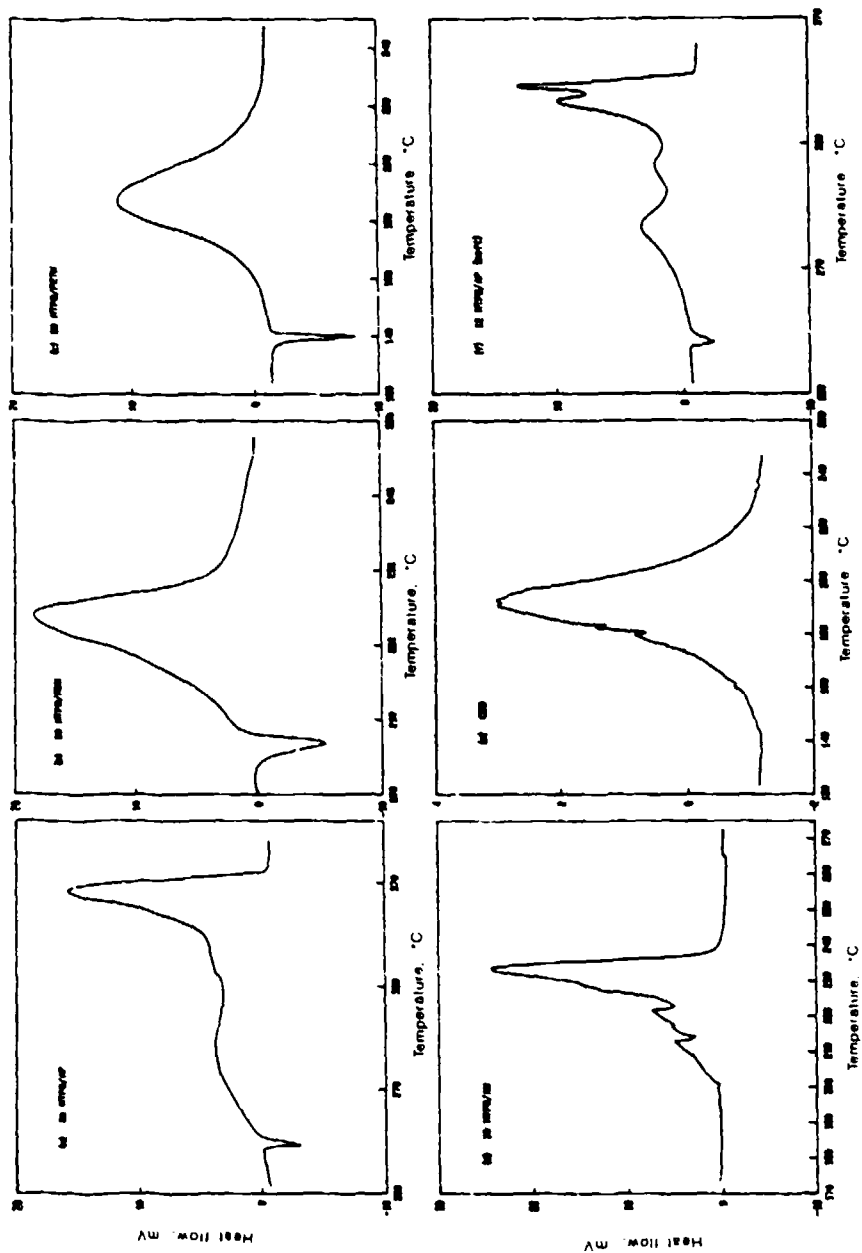


Figure 10: DSC curve obtained at ambient pressure and $5^{\circ}\text{C min}^{-1}$. (a) HTPB/AN (20/80), (b) HTPB/AN (20/80), (c) HTPB/AN (20/80), (d) HTPB/AN (20/80), (e) CDB, (f) Soft HTPB/AN (12/88)

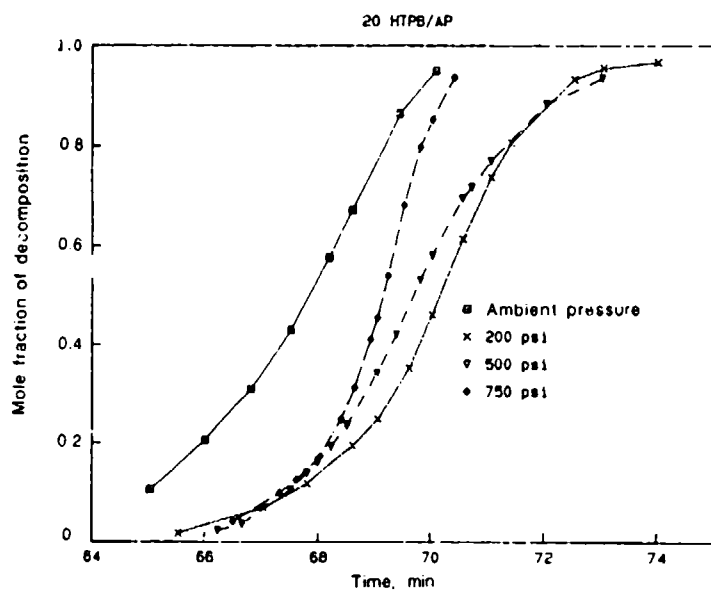
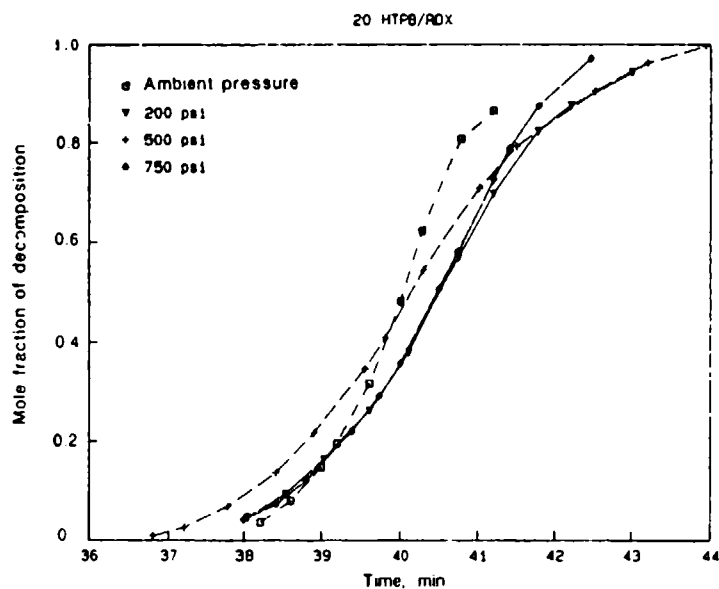


Figure 11: Degree of decomposition as a function of time at various pressures (a) HTPB/RDX (20:80), $5^{\circ}\text{C min}^{-1}$, (b) HTPB/AP (20:80), $5^{\circ}\text{C min}^{-1}$

Decomposition vs. time curves at various pressures for the HTPB/RDX (20:80) and HTPB/AP (20:80) propellants are illustrated in 11a and 11b. The sigmoid-type curves for the HTPB/RDX (20:80) propellant (Fig. 11a) are typical of thermal decomposition of pure RDX in the solid-state [16]. Increasing the pressure from ambient to 1.7, 3.4 and 5.2 MPa, at a heating rate of $5^{\circ}\text{C min}^{-1}$, did not alter the reaction rate of this propellant nor the shape of the curves, indicating that there was no change in the decomposition mechanism when the pressure increased from ambient to 5.2 MPa.

The rates of decomposition for the HTPB/AP (20:80) propellant decreased with increasing pressure, in the pressure range 0.1 to 5.2 MPa (see Fig. 11b), consistent with a unimolecular-type reaction mechanism [16]. There was no change in the general shape of the curve, i.e. there was no change in the decomposition mechanism with an increase in pressure up to 5.2 MPa.

Table 6: Kinetic parameters of propellants (ambient pressure)

Propellant Type	Heating Rate ($^{\circ}\text{C min}^{-1}$)	Reaction Order	Activation Energy (kJ. mol $^{-1}$)	ln A (s $^{-1}$)
HTPB, AP (20:80)	5	1 ± 0.2	406 ± 150	70.5
	20	0.6 ± 0.2	131	76.3
Hard HTPB/AP (12:88)	5	0 ± 0.2	224 ± 80	36.5
	20	0 ± 1.0	296 ± 100	175.2
Soft HTPB, AP (12:88)	5	0.6 ± 0.4	409 ± 100	75.2
	20	0 ± 0.5	73	41.2
HTPB, RDX (20:80)	5	1.0 ± 0.1		93
HTPB, PETN (20:80)	5	1.2 ± 0.3	170 ± 30	39
HTPB, AN (20:80)	5	1.1 ± 0.2		146
	20	0 ± 0.2	172	99
CDB	5	1.3 ± 0.4	182	41.8
	20	1.0 ± 0.2	190	133

Kinetics of Thermal Decomposition

The kinetic parameters of the propellants studied here, evaluated by multilinear regression analysis of equation (3), at heating rates of 5 and $20^{\circ}\text{C min}^{-1}$ and pressures from ambient to 5.2 MPa are listed in Table 6. In general, there was little change in the kinetic parameters with a change in pressure from ambient to 5.2 MPa.

For the HTPB/AP (20:80), HTPB/PETN (20:80) and HTPB/RDX (20:80) propellants, the overall reaction order, at a heating rate of $5^{\circ}\text{C min}^{-1}$, is unity. This is consistent with isolated reactions in the solid phase. The reaction order for the decomposition processes of these propellants is probably a composite order from a number of reactions such as decomposition of binder, oxidiser, and their products.

When the oxidiser loading level was increased from 80 to 88 weight % (viz. the hard and soft HTPB/AP (12:88) propellants), the reaction order, based on a reaction order described by equation (1), changed to zero, indicating that the rate of reaction is not solely dependent on the amount of unconsumed propellant. The apparent zero order kinetics are consistent with the general observation that the decomposition of some explosives and energetic materials is zero order [17].

Changing the heating rate from $5^{\circ}\text{C min}^{-1}$ to $20^{\circ}\text{C min}^{-1}$ did not alter the reaction order but in general, decreased the activation energy, i.e. the reaction mechanism was not altered but the decomposition rate increased. Our results suggest that in modelling fast and slow cookoff reactions, it is important to determine the kinetic parameters at the appropriate heating rates. However, in the pressure range studied here, pressure has a less important effect on the kinetic parameters and reaction mechanisms. Further work on the effect of increasing heating rates (above $20^{\circ}\text{C min}^{-1}$) and pressures (above 5.2 MPa) will be reported in a later paper.

4. Conclusions

A modified SSCB test methodology, by which the energy (pressure) output can be determined, has been developed at EOD to assess the cookoff response of rocket propellants. Modification of the standard SSCB apparatus did not alter the test response, reaction temperature, and reaction time. The modified SSCB test is useful in discriminating between propellants which responded with similar damage to the test assembly and gives a more quantitative measure of the reaction violence.

The cookoff response of a series of in-service and research composition rocket propellants have been ranked using the standard and modified SSCB test. Hazard criteria for cookoff response of propellants should include some indication of when to expect a reaction, i.e. reaction time and temperature, in addition to the severity of the response. The AN-based and CDB propellants gave less violent responses but were much easier to initiate. The AP-based propellants were generally very hard to initiate (relatively long reaction times) but gave more violent responses. Increasing the plasticizer level of the HTPB/AP (12:88) propellant moderated the test response.

The HTPB/RDX (20:80) propellant showed a marked difference in the test response when the heating rate was changed. At the fast heating rate, the temperature difference between the outer surface and centre of the propellant was almost 100°C , whereas at the slow heating rate, almost uniform temperature distribution was achieved after the first 30 minutes. The heating rate and propellant geometry determine the temperature distribution across the sample and therefore govern where the cookoff begins and consequently, the reaction violence.

The results from this study indicate that the reaction violence of propellants is governed to a large extent by their thermomechanical properties during cookoff, and Dynamic Mechanical Thermal Analysis is a useful and a quick means of determining the thermomechanical properties, viscosities, and phase changes of the propellant with temperature.

On the other hand, the reaction time and temperature of propellants during cookoff are governed by the thermochemistry, such as thermal stability and

decomposition kinetics. Propellants with low thermal stability are easiest to initiate. Heating rate has an important effect on the kinetic parameters and therefore cookoff response. A change in heating rate from $5^{\circ}\text{C min}^{-1}$ to $20^{\circ}\text{C min}^{-1}$ increased the decomposition rate in all the propellants. However, pressure (in the range 0.1 to 5.2 MPa) has a less important effect on the kinetic parameters and reaction mechanisms.

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Correlation of Cookoff Behaviour of Rocket Propellants with Thermomechanical
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AUTHOR(S)

S.Y. Ho, T. Ferschl and J. Foureur

CORPORATE AUTHOR
DSTO Materials Research Laboratory
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Thermomechanical propertiesThermochemical properties
Cast double base propellants

ABSTRACT

The fast and slow cookoff behaviour of a series of in-service and research composition rocket propellants have been evaluated using the standard SSCB (based on the NWC design) test, as part of a program in Explosives Ordnance Division (EOD) to develop an extensive insensitive munitions technology base. A modified SSCB test methodology, whereby the pressure output can be measured, was developed to enable a more quantitative measure of the reaction violence and to provide further insight into the cookoff mechanism. The temperature distribution/gradient at various positions and depths in the cylindrical propellant specimen, during fast and slow cookoff, were measured, in order to understand the marked difference in the severity of the response shown by some of the propellants when the heating rate was changed. Pressure and heating rate dependent thermochemical properties and thermomechanical properties of the propellants were measured and correlated with cookoff behaviour.

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S.Y. Ho, T. Ferschl and J. Foureur

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